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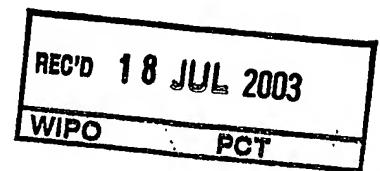


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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. PS 3292 for a patent by CAST CENTRE PTY LTD as filed on 01 July 2002.

WITNESS my hand this  
Eighth day of July 2003

JULIE BILLINGSLEY  
TEAM LEADER EXAMINATION  
SUPPORT AND SALES



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**PROVISIONAL SPECIFICATION**

Invention Title: **Coatings for articles used with molten metal**

The invention is described in the following statement:

## COATINGS FOR ARTICLES USED WITH MOLTEN METAL

### Technical Field

This invention relates to coatings for articles used in handling molten metal. It also relates to a process of providing such articles with an improved coating.

### 5 Background of the Invention

PCT/AU00/00239 discloses coating compositions useful in low pressure and gravity die casting. The surface of each metal mould or die component, which is contacted by molten metal, is provided with a mould or die coating. Under previously known procedures, a ceramic-based coating was used at a thickness of 10 from about 0.05 to 1.0mm. By referring to the coatings as "ceramic based" the term "ceramic" was used in its art recognised sense as being inorganic, non-metallic materials processed or consolidated at higher temperature" (McGraw-Hill Encyclopaedia of Science and Technology 1994). The classes of materials generally considered to be ceramics include oxides, nitrides, borides, silicides and 15 sulfides. Intermetallic compounds such as aluminates and beryllides are also considered as "ceramics" as are phosphides, antimonides and arsenides. The main function of the ceramic based coating was to provide a degree of insulation which was intended to prevent premature solidification of the molten metal, and thereby enable the complete filling of the die cavity before solidification started. However, 20 the coating also protected the die surfaces from erosion or corrosion by impingement by or contact with molten metal. To reduce thermal expansion mismatch between ceramic coating and the steel die, it was preferable to apply a bond coat to the die surface before application of the die coating.

The known die coating technology typically involved the use of a water-based suspension of ceramic particles in a water-based binder, most commonly sodium silicate. Coating mixtures of this type needed to be properly stored. Stirring and testing was required to prepare them for use and this was inconvenient. The coating was applied to the prepared surface of a die component using a pressurised air spray gun. For this, the die component was preheated, typically from about 150

to 220°C, such that water was evaporated from the die surface, enabling the binder to polymerise and bond the ceramic particles together and to the die surface.

In PCT/AU00/00239 an improved die coating for use on the surface of a mould or die component contacted by molten metal in low pressure or gravity die casting was disclosed. The coating included a porous layer of ceramic material produced by co-deposition, using a thermal spraying procedure, of a powder of the material and a powder of a suitable organic polymer material and, after the co-deposition, heating of the polymer material to cause its removal. In that specification the term "ceramic material" was used very broadly but consistent with the definition, outlined earlier, in this technology field.

That invention also provided a process for providing a die coating on such surface of a metal mould or die component wherein an initial coating of organic polymer material and ceramic material was formed on the surface by co-deposition of powders of the materials by a thermal spraying procedure, and the initial coating was heated so as to remove the polymer material and leave a porous coating of the ceramic material. To reduce the thermal expansion mismatch between metal die and the coating, a bond coat such as that described below was applied between the coating and the metal die surface. The bond coat also served to enhance the adhesive strength of the coating. The bond coat powder that was particularly effective was a Metco 480-NS grade fully alloyed spheroidal, gas atomised Nickel 95% Aluminium 5% for which the data sheet indicated a particle size range of not more than 90 $\mu$ m and not less than 45 $\mu$ m. Other commercially available bond coats and also mixture of metals and ceramic bond coats can be used.

We have now found that coating compositions as disclosed in this PCT patent application may surprisingly be extended beyond the use in dies described in that invention to liquid metal transport and holding articles. In particular, we have found that the coating compositions may be usefully applied to transfer troughs, launders, ladles, skimming tools and siphon tubes. It may also be used in Direct Chill Casting for coating hot tap refractory such as thimbles, orified plates, dummy block, ingot moulds, filter boxes and riser tubes. The coating composition may also

be used to coat metal thermocouple sheaths in cast houses, furnaces and mineral processing and chemical plants. Indeed the coating composition can be usefully employed on a wide range of chemical engineering applications where metal surfaces are coated. Examples include tankers and mixing equipment used in  
5 chemical and petrochemical plants.

We have also found that as well as thermal spraying procedures as disclosed in PCT/AU00/00239 that other application techniques may be used including high velocity oxy fuel (HVOF) .

#### **Summary of the Invention**

10 This invention provides in one form an improved coating for use on articles in contact with molten metal, but excluding low pressure or gravity die coating, the coating including a porous layer of ceramic material produced by co-deposition of a powder of said ceramic material and a powder of a suitable organic polymer material and, after the co-deposition, heating of said polymer material to cause its  
15 removal. A bond coat as described above is preferably used between the article and the coating.

20 Preferably the ceramic powder is selected from at least one metal compound such as oxides, nitrides, carbides and borides, preferably from the group comprising alumina, titania, silica, stabilised zirconia, silicon nitride, boron nitride, silicon carbide, tungsten carbide, titanium borides and zirconium boride.

Preferably the ceramic powder is selected from at least one mineral compound such a clay minerals, hard rock ore and heavy mineral sands such as those of ilmenite, rutile and/or zircon.

25 Preferably the organic polymer powder is formed from a thermoplastic material, such as polystyrene, styrene-acrylonitrile, polymethacrylates, polyesters, polyamides, polyamide-imides and PTFE.

Preferably the ceramic and polymer powders are of relatively narrow size spectrum and preferably in the range 20 $\mu$ m - 400 $\mu$ m.

Preferably the ceramic and polymer particles are of particle sizes not more than about 300  $\mu\text{m}$  and not less than about 5  $\mu\text{m}$  in the case of said ceramic powder and not less than about 45  $\mu\text{m}$  in the case of the polymer powder.

5 Preferably a substantially uniform die coat is provided over all surfaces of the metal article.

Preferably said coating having a thickness of from about 50 to 600  $\mu\text{m}$ .

More preferably said coating having a thickness of from about 200 to about 400  $\mu\text{m}$ . The insulating properties of the coating are a function of the coating thickness as well as the porosity of the coating.

10 The invention provides a process or providing a die coating on the surface of an article that comes into contact with molten metal, wherein an initial coating or organic polymer material and ceramic material is formed on the surface by co-deposition of powders of the materials and the initial coating is heated so as to remove the polymer material and leave a porous coating of the ceramic material. In  
15 order to produce a very smooth surface finish, an outermost layer of fine ceramic material without polymer can be applied. This is particularly useful where the die coating is more porous.

In an alternative form the invention provides an improved coating for use on metal articles that are in contact with molten metals. The improved coating  
20 including a porous layer of ceramic material produced by co-deposition of a powder of said ceramic material and a powder of a suitable organic polymer material and, after the co-deposition, heating of said polymer material to cause its removal.

Preferably a bond coat is applied to the metal articles before the improved coating is applied.

25 **Detailed Description of the Invention**

The invention will now be described by reference to the following non-limiting example.

**Example 1**

A Bond coat was applied to a prepared metal surface with a Miller Thermal  
30 SG 100 Plasma Spray Torch thermal spray unit. The bond coat powder was a

Metco 480-NS grade fully alloyed spheroidal, gas atomised Nickel 95% Aluminium 5% for which the data sheet indicated a particle size range of not more than 90 $\mu\text{m}$  and not less than 45 $\mu\text{m}$ . The process settings used were as follows: -

5      Voltage:                    33  
      Current:                    650  
      Plasma Gases:            Argon at 50 psi & Helium at 50 psi  
      Powder Feed Rate:       11.5 RPM at 35 psi  
      Spray Distance:           100mm

10     Ceramic powder and polymer powder were mixed and subjected to a thermal spraying to form a co-deposited coating on a ladle used for transferring molten metal to a die cavity defining the surface of a low pressure metal die cast component. The ceramic powder was Metco 210 (NS/NS-1/NS-1-G) grade zirconia stabilised by 24% magnesium oxide for which the data sheet indicated a particle size range of not more than 90 $\mu\text{m}$  and not less than 11 $\mu\text{m}$ , a melting point of 15 2140°C and a density of 4.2gcm<sup>-3</sup>. The polymer powder was of polymer supplied by Sulzermetco which had been ground to -150 + 45  $\mu\text{m}$  (-100 +325). The powder mixture of MgO(24%) ZrO<sub>2</sub>/polystyrene contained 15 % volume percent (3wt%) of polymer.

20     The co-deposition of the powder mixture was performed using a Miller Thermal SG 100 Plasma Spray Torch and a Miller Thermal powder feeder, under the following settings:

25     Voltage:                    34  
      Current:                    750  
      Plasma Gases:            Argon at 50 psi & Helium at 50 psi  
      Powder Feed Rate:       2.88 (rpm) at 35 psi  
      Spray Distance:           100 mm

30     Following co-deposition of the blended powders, the deposited coating was heated to 420°C for one hour to cause the polymer to decompose. Polymer decomposes fully at 320 to 350°C in air. The porous, stabilised zirconia coating resulting from removal of the polymer by de-composition was found to comprise an

excellent coating having good abrasion resistance enabling it to withstand the impingement of molten metal. The coating also exhibited a low heat transfer coefficient, such that solidification of molten metal during such molten metal handling operations was able to be delayed until molten metal had been transferred.

5 Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It will be understood that the present invention encompasses all such variations and modifications that fall within the spirit and scope.

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